FACULTY OF TECHNOLOGY

REMOBILIZATION OF BOUND ARSENIC AND ANTIMONY IN A FLOW-THROUGH COLUMN EXPERIMENT WITH PEAT SOIL

Vera Amanda Luostarinen

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ABSTRACT

Remobilization of bound arsenic and antimony in a flow-through column experiment with peat soil

Vera Amanda Luostarinen

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Supervisors at the university: Katharina Kujala & Uzair Akbar Khan

Treatment peatlands have been used to purify mine water for years in Finland. In terms of sustainability in mining industry it is important to know what happens to bound contaminants: Do they stay bound or do they start leaching to nature?

This Master Thesis project involved the following research methods: setup and maintenance of flow-through peat columns, sampling inflow, outflow and porewater, analysis of arsenic and antimony using colorimetric methods, dissecting the peat column and determining bound arsenic and antimony concentrations in peat and interpretation of results.

The main hypothesis in this project was: Does reduced arsenic/antimony concentrations in inflow water lead to remobilization and redistribution of the bound contaminants in the peat columns observable as a flattening off and traveling of the peak concentration of bound contaminant. In this thesis the goal was to find out three things:
First, is there a clear binding pattern for arsenic and antimony in the peat, i.e., do we see areas with high arsenic/antimony concentrations or is there an even distribution? Second, does remobilization occur when the inflow water quality changes?
And last, how does the distribution of arsenic and antimony in the peat column change throughout the remobilization experiment?

The most important finding of this study is that once the inflow water was diluted to low concentration leaching of both arsenic and antimony increased compared to the high concentration of the inflow water. These results also support previous research that there is an increased risk of contaminant leaching after mine closure. These results can be used to get a better understanding how arsenic- and antimony-loaded treatment peatlands should be managed and the risks in leaching even prevented. In general changes in inflow water quality, as may be expected after mine closure, may result in remobilization and subsequent leaching of the bound contaminants.

Keywords: peatlands, mining, arsenic, antimony, wastewater

FOREWORD

I would like to dedicate this effort to my mom and dad, as they remain the biggest influence on my life, you two have made me into such a strong woman. Thank you for your everlasting love, academic support and showing me "You can achieve anything if you really want to. The sky's the limit.''

I would like to thank Water, Energy and Environmental Engineering Research Unit for offering an interesting and relevant thesis topic. My supervisors at the university were Katharina Kujala and Uzair Akbar Khan. Thank you for your guidance, thoughts and valuable comments regarding the content of the work. I wish you both all the best and wish you keep continuing to contribute in the research field for an important matter.

During this project, I have had the pleasure and privilege to be part of the Water Resources and Environmental Engineering Research Group. I want to express my sincerest gratitude of discussions and exchange of thoughts with you. Each discussion has further enlarged my understanding and perspective to the issues at hand. Especially the site visit to Kittilä mine in August 2020 was very educational and valuable.

This study was carried out at the Water, Energy and Environmental Engineering Research Unit in the University of Oulu with the funding provided by K.H. Renlund Foundation. I would like to thank also the Finnish foundation Maa- ja vesitekniikan tuki ry for supporting the work. The contribution is acknowledged and immensely appreciated.

Despite the exceptional circumstances in year 2020 of COVID-19, I have enjoyed my time working on my thesis, learning so much and discovering new things to learn of.
Warmest thanks to two amazing grandmothers in my life. Salme, I'm forever grateful for motivating me pushing forward my studies. Leena, I am so honored that ever since beginning my studies you have said that Environmental Engineering is the future. Grandfathers, thank you for teaching me to live my life with positive mind-set. Thanks for all my family and wonderful friends.

Lastly, thank you Jussi. I'm so lucky to call you mine and honored of all you do for me. I love you.

Espoo, 11.05.2021

Vera Amanda Luostarinen

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LIST OF ABBREVIATIONS

As	Arsenic
Fe	Iron
ICP-MS	Inductively coupled plasma mass spectrometry
ISO	International Organization for Standardization
KH_2PO_4	Potassium dihydrogen phosphate
Mn	Manganese
MQ	MilliQ Water
Ni	Nickel
RPM	Revolutions per minute
Sb	Antimony

1 INTRODUCTION

Mineral resources are needed today in the modern world. Mining is a way to generate mineral resources and has become a major industry in the last century (Younger et al. 2002). Mining is an industry that produces the necessary raw materials for many industries e.g. metal, chemical and paper industries, agriculture, and numerous other industries. Mining inevitably affects its environment (Nordstrom, 2011). Prevention of negative environmental impacts requires the application of Best Available Techniques (BAT) to extractive activities, from mineral exploration and mine design — through the life cycle of the activity — to mine closure and aftercare.

Mining-affected waters contain many contaminants such as sulfate, nitrogen, and metals/metalloids. Treatment peatlands can be used to remove these contaminants from mining-affected water. The treatment peatlands in Kittilä, Lapland have removed arsenic and antimony rather well in the past, but as they have been in use for 10-12 years, arsenic and antimony have accumulated in the peat. Changes in inflow water quality (as may be expected e.g. after mine closure) may result in remobilization and subsequent leaching of the bound contaminants (Palmer et al. 2015; Khan et al., 2019, 2020). However, it is not clear if and how remobilization occurs in arsenic- and antimony-loaded treatment peatlands.

The main hypothesis in this project was:
Reduced arsenic/antimony level in inflow water will lead to remobilization and redistribution of the bound contaminants in the peat columns which will be observable as a flattening off and traveling of the peak concentration of bound contaminant.
From this hypothesis, the following research questions were derived:

1) Is there a clear binding pattern for arsenic and antimony in the peat, i.e., do we see areas with high arsenic/antimony concentrations or is there an even distribution?
2) Does remobilization occur when the inflow water quality changes?
3) How does the distribution of arsenic and antimony in the peat column change throughout the remobilization experiment?

Due to fact that it is difficult and challenging to study remobilization of contaminants in the field, a column experiment was set up in the laboratory to simulate remobilization of

bound arsenic and antimony. Peat columns were preloaded with arsenic and antimony and the pattern of remobilization and leaching was studied.

Setup and maintenance of flow-through columns involved building the columns and making sure they operate smoothly during the experiment. During the experiment sampling was done regularly from inflow, outflow and porewater. Sampling was followed by analysis of arsenic and antimony using colorimetric methods. Lastly this project involved dissecting the peat column and extracting bound arsenic and antimony. Interpretation of results of the project is discussed in chapter five.

2 PEATLANDS AND THEIR USE FOR TREATMENT OF MINING-AFFECTED WATERS IN LAPLAND

2.1 Overview

Wetlands have been utilized in municipal wastewater treatment since the 1970s and in the 21st century also for industrial waters. For industrial wastewater the wetlands have mainly been used for mining waters. (Ronkanen, 2009). The wetland's cleaning efficiency is based on the biological, chemical, and physical processes taking place there and the slow flow rate of water, which allows solid matter to settle in the wetland (Räisänen, 2004). In mines, the wetland treatment of wastewater is usually the last step in water treatment before the water is returned to the natural cycle. The wetland's cleaning efficiency and operation is monitored by the authority and the mining company in order to assess the environmental impact of the mining industry.

Some of Finland's metal ore mines use wetland treatment as part of the treatment of the water that is removed from the mine's cycle into nature. The wetland retains solids, metals, and nutrients while the water to be cleaned flows through it. As wetland treatment is the last water purification process in the mines that exploit it before the mine water is discharged into the environment, monitoring the wetland's cleaning efficiency is very important. If the treatment of water discharged from the mine into the environment has not been sufficient, the consequences may manifest themselves, for example, as acidification of the mining environment or eutrophication of the water body (Kauppila et al., 2011).

The mining industry is a major industry in Finland. There are 9 active metal ore mines and 29 other mines in Finland (Vasara, 2018). Mining minerals include metal ores, industrial minerals, industrial stones, soap stones, and jewelry and precious stones.

Mining has a wide range of effects on the environment, e.g. due to landscape changes and operational emissions. Water is one of the main routes for pollutants from mining to enter the environment. The most significant environmental impacts are usually related to the extraction of sulfide metal ores. (Ramboll Finland Oy., 2015)

2.2 Peatlands

A wetland is defined as a body of water where the water level is above or close to the surface for at least part of the year (Cooper, 2003). Examples of wetlands include swamps, marshes, bogs, wet meadows, tidal meadows, floodplains, and estuarine strips. Wetlands meet the ecosystems of water and dry land; they contain both terrestrial and aquatic plants (Räisänen, 2004). The vegetation is often lush, which provides good growing conditions for microorganisms. Wetlands are dominated by plant species that are well adapted to wet conditions and tolerate continuous or intermittent anoxia or low oxygen. (Kadlec & Knight, 1996)

Wetlands can have very different soils. The most common wetlands in Finland are bogs, where weakly decomposed organic matter is deposited, forming a low-nutrient and acidic growing medium for marsh plants. Peat comes from parts of dead plants that, under very humid conditions, result in incomplete decomposition of organic soil. Decomposition is incomplete due to lack of oxygen, in which case the plants do not decompose properly but are deposited as growing layers of peat. Peat is a material in which more than 75% of the dry matter contains organic matter. Peatland, on the other hand, is classified as land with a peat layer over 30 cm thick. Peat soil can occur with or without vegetation cover. (Turveteollisuus ry, 2001) The Figure 1 shows a picture of peatland in Kittilä, Lapland. From the picture of the peatland can be seen that there are areas in the peatland that are very wet, and open water is visible.

Figure 1. Treatment peatland in Kiistala, Kittilä (Photo by: Luostarinen, 2020).

2.3 Mine water

Mine waters typically contain sulfate (SO_4^{2-}) minerals, metalloids (nickel (Ni), arsenic (As), lead (Pb), antimony (Sb), nitrogen (N) compounds, SO_4^{2-}, and other contaminants such as carboxymethylcellulose, phosphate (PO_4^{3-}), oil, xanthates, and salts. These can come from mineral ore, process chemicals, and explosives (Kauppila et al., 2011). Antimony, nickel and arsenic are amongst the most important pollutants for the water load of the Kittilä mine (Ramboll Finland Oy., 2015).

2.4 Antimony

Antimony is a much rarer substance in the earth's crust than arsenic, but usually co-occurs with arsenic. Antimony concentrations measured in stream waters are usually very low, but little information is available on the concentrations (Lahermo et al., 1996). Antimony is a metallic element belonging to the nitrogen group of the periodic table. Antimony is present everywhere in the environment as a result of natural processes and human

activity. Antimony exists mainly as Antimony(III) and Antimony(V) in environmental, biological and geochemical samples (Filella et al., 2002; Koljonen, 1992). Antimony is a lustrous, silvery, bluish white solid that is very brittle and has a flaky texture. It occurs chiefly as the gray sulfide mineral stibnite (Sb_2S_3). The geochemical properties are similar to those of the related elements arsenic and bismuth. Antimony is used in semiconductor technology in the manufacture of infrared detectors and diodes. Antimony can also be used as an oxide in fire-resistant substances (Cooper 2003). Antimony has no role as a nutrient. Antimony and its compounds are toxic. In Finland the domestic water must not contain more than five micrograms of antimony per liter (STM 461/2000). Soils and sediments have gained elevated concentrations of antimony either from anthropogenic sources or from high arsenic concentrations in sulfidic ores. In current knowledge on information available antimony appears to be highly unreactive in soils (Filella et al., 2002; Koljonen, 1992).

High antimony concentrations are commonly associated with high arsenic concentrations in sulfide ores. Antimony is therefore obtained from the extractive industry in connection with various sulphide ores as a by-product. Antimony concentrations can also be considered a kind of radar for finding gold in the area (Filella et al., 2002).

2.5 Arsenic

The principal routes of exposure to arsenic are food and drinking water (WHO, 2011; IARC, 2012) . Arsenic is the most common gold companion element after sulfur. It tends to enrich its background value up to several times in the vicinity of gold ores. Regionally in Finland the arsenic content of organic sediments in moraine, spring waters and springs is clearly related to gold deposits (Lahermo, 2004).

The concentration of arsenic in the soil is very high in some places and can dissolve in groundwater and enter the boreholes. In Finland arsenic is most abundant in the soil in the Pirkanmaa region, and in some places also in other parts of south-eastern, southern and south-western Finland. In the Figure 2 is shown distribution of total arsenic concentrations in Finland.

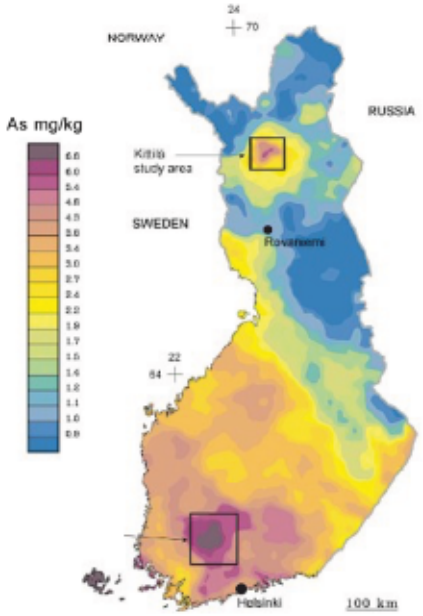

Figure 2. Distribution of total arsenic concentrations in the fine fraction (< 0.06 mm) of till. The Kittilä study area in central Lapland is marked and was also the study site in this project (Koljonen, 1992).

The typical concentration of arsenic in groundwater water is less than 0.1 micrograms per liter (µg/l). However, its maximum concentrations can be well above 100 µg / l. The Ministry of Social Affairs and Health (STM) does the planning, guidance and implementation of health and social policy in Finland. STM has set that, in Finland, the maximum permissible concentration of arsenic in drinking and domestic water is 10 µg/l (STM 461/2000).

Constructed wetlands are capable of removing arsenic. The main removal mechanisms in wetlands are precipitation, coprecipitation and sorption (Vymazal, 2007). In addition to that bacteria can mediate these removal processes under favorable conditions. Factors that affect arsenic speciation include pH, dissolved oxygen (DO), iron (Fe), sulfur (S), phosphorous (P), total organic carbon (TOC) and wetland media. To improve wetlands design the knowledge of the different processes involved is required. (Lizama Allende et al., 2011; Mattes et al., 2004)

3 IMPACTS OF ARSENIC, ANTIMONY & MINING

3.1 Impact on human health

Arsenic in drinking water is a global problem and its health effects have been extensively studied. Arsenic is a human carcinogen (IARC, 2012) and is harmful to health. Arsenic is the most common gold companion element after sulfur (Lahermo, 2004).

Arsenic in drinking water can cause e.g. bladder cancer and skin and lung cancer. There is no safe limit for the intake of arsenic in food (IARC, 2012). According to studies (EFSA, 2009), the link with bladder cancer is noticeable, even if the arsenic concentration in the well water is lower than the maximum permissible concentration of 10 µg/l. The risk of cancer clearly increases when the arsenic content of drinking water exceeds 150 µg/l. The European Food Safety Authority has estimated that a human exposure to arsenic of 0.3 to 8 µg/kg bw/day throughout their life increases the risk of cancer by up to 1% (EFSA, 2009).

Antimony is a toxic chemical element. The use of antimony in industrial applications has increased significantly in the recent decades. Studies of antimony have focused primarily on the determination of Antimony (III) because Antimony (III) compounds are ten times more toxic than Antimony (V) compounds. Antimony (III) is particularly dangerous due to its irreversible binding to thiol-containing enzymes. Antimony (III) also binds to erythrocytes and intracellular thiol groups. Antimony (V) does not have the same property. (Amereih et al., 2005) Antimony trioxide is possibly carcinogenic to humans (Sundar & Chakravarty, 2010). Thus Antimony (III) compounds such as antimony trioxide can cause lung cancer if inhaled (Amereih et al., 2005).

3.2 Environmental and social impact of mine

Mining has significant social impacts at all stages of its operations, which sometimes also provoke heated public debate. The social impacts are significantly project-related multiplier effects and thus differ in nature from other impacts of mining, mainly based on measurable scientific information. The nature and significance of the social impacts of mining are affected not only by the size and location of the mine, but also by the quality

of the information flow and dialogue between the mining company and the stakeholders in the affected area. The biophysical and socio-economic changes that give rise to the social multiplier effects of mining are often repeated in exactly the same way shown in the Table 1.

Table 1. Biophysical and socio-economic change processes often associated with the commencement of mining operations (Kauppila et al., 2011).

Biophysical changes	Socio-economic changes
Land and water • *Protection of natural values* • *Protected areas* • *Protected plant species* • *Fauna to be protected* • *Surface and groundwater* • *Landscape effects* • *Noise and dust* • *Pollution of nature* • *Water pollution* • *Traffic pollution*	Settlement • *Changes in settlement* • *Placement of new settlement* • *Formation of a mining community* Industry • *Revival of business life* • *Changes in current industries* • *New industries and companies* Economics • *Service level change* • *Development of tax revenues* • *Prosperity, increase in well-being* Employment • *Employment growth* • *Indirect jobs* • *Training needs related to mining*

In the mine's proximity, the impacts are on the pursuit of livelihoods, comfort and the use of nature for domestic and recreational purposes. The effects are caused by e.g. increasing traffic, noise, dust, flue gases, vibration and wastewater. Further away from the mining area itself, mainly at the municipal level, the positive economic and employment effects are emphasized. They are targeted at almost all citizens through various multiplier and indirect effects and the strengthening of public finances. The increase in workers and population brought about by the mine will affect the local way of life and improve the supply and availability of municipal and commercial services. (Kauppila et al., 2011)

During the exploration and construction phase of the mine prior to the construction of the mine, the uncertainty of the local residents and the "Not In My Back Yard", or NIMBY

thinking, which is mainly understood from an economic point of view, are emphasized. In Finland, especially in connection with uranium exploration, there has also been a total opposition to the commencement of mining operations, which is referred to as BANANA (Build Absolutely Nothing Anywhere Near Anybody) (Kauppila et al., 2011).

Almost without exception, a permanent mining community has been established in connection with the mines that previously operated in Finland. Therefore, there is still uncertainty and concern about the demographic impact of the mining project and what a new community with potential social problems will form in the area.

During mining, the social impact of a project is always related to the target community and the wider social fabric of the area. The effects can be direct, such as economic and employment effects or the prevention of land use from other activities as land is transferred to mining activities (e.g. in reindeer areas). Impacts can also be indirect, such as impacts on recreational use in an area due to changes in the environment (Kauppila et al., 2011).

Depending on the location of the mine and e.g. shift arrangements, different requirements arise regarding the location and permanence of the settlement needed by the mine workers. The social effects are decisively different in these circumstances. With regard to work and settlement arrangements, it must be clarified whether development is solely determined by demand or supply, and what division of roles between the municipality and the company is in the plan (Kauppila et al., 2011).

4 MATERIALS AND METHODS

The retention of arsenic and antimony in the peat columns could be inferred from the colorimetric determination of arsenic and antimony concentrations in inflow and outflow. When the removal efficiency of the columns started to decline, the inflow water containing high concentrations of arsenic and antimony was switched to inflow water that has lower concentration of arsenic and antimony.

The research process included five steps. i) The material of peat and water samples were taken from the study site that was a mine-water treatment peatland in Kittilä, Finland. ii) Eight different columns were setup for the flow-through column experiment. iii) Concentration in inflow, outflow and porewater was monitored as the columns was loaded with arsenic and antimony. iv) Water was switched to low concentration water and inflow, outflow and porewater concentration was monitored. v) Columns were deconstructed and accumulation of arsenic and antimony in peat was measured.

4.1 Study site

The study site is located in central Lapland and is dominated by extensive aapa bogs, which cover up to about 60% of its area, as well as valleys of large rivers. To the west are the Tornionjoki-Muonionjoki and Ounasjoki rivers, and to the east are the Kemijoki tributaries Kitinen, Luiro and Kemihaara. There are a few natural lakes, but in the northern parts of the area are the large Loka and Porttipahta artificial lakes. Both extensive wetlands and artificial lakes have their own impact on the climate of the area, as they balance the thermal conditions of the growing season. There are also fells in the whole area, the highest in the west is Yllās and Pallas, and the highest in the northeast in the southern parts of Sokosti Saariselkā. The area is the most continental in our country, as it is located far from both the Gulf of Bothnia and the Arctic Ocean (Kersalo & Pirinen, 2009).

The average annual temperature in the whole area is already slightly on the frosty side, varying between less than -1 degree in the southernmost parts and almost -2 degrees on the northern edge of Kittilä and Sodankylä. January is usually the coldest month here in the clear continental climate; the average temperature in January is -13.5 ° C in the

southern parts of the region and -14.5 ° C in the northern parts. The coldest area of Finland is the northern river valleys of Muonio and Kittilä. The average temperature in July is mostly 13.5 ° C, with the warmest in the river valleys of the southern parts and the coolest in the high fells of the northern parts (Kersalo & Pirinen, 2009).

The annual average rainfall is 450–550 mm in most parts of the study area, and about 600 mm on the southern edge of Saariselkä. Average annual rainfall increases from northwest to southeast. The driest areas are the valleys of Ounasjoki and Kitinen. Higher rainfall occurs especially in southern Saariselkä and the Yllās-Pallas mountain range. Orography has a significant impact on rainfall in the area depending on the prevailing wind direction. Spring is quite often the driest season with April as the driest month, although February and March are roughly equally dry; rainfall averages 25-30 mm. In July and August, average rainfall is 60–70 mm in each month. It should be noted that almost half of the annual rainfall i.e. 250-300 mm is takes place as snow (Kersalo & Pirinen, 2009).

The study site comprises two wastewater treatment peatlands: one receiving pretreated process wastewater (peatland A) and the other subjected to pretreated drainage water (peatland B) from the mine. The mine is located in northern Europe, in Finland. The location is in Finland in an area called Kittilä in Lapland. Kittilä mine is one of the largest gold mines in Europe. Kittilä mine is operated by Agnico Eagle Oy. Finland, a subsidiary of Canadian gold mining company Agnico Eagle Mines Limited. Starting operation in 2008, the mine is extracting ore from one of the largest European deposits which is expected to last till 2036. (Agnico Eagle, 2013)

The peat samples for the flow-through column experiment were from the site in Kittilä, Finland in the fall 2019. Peat samples were stored in a cool and dry place inside the cold room at temperature of 4°C prior to start of the tests in the spring 2020.

4.2 Construction of columns

The columns were built for flow-through column experiments under laboratory conditions in the University of Oulu. All operating columns were filled with surface-layer peat from treatment peatland A. The bottom and the top of the columns were filled with quartz sand. Lastly, the columns were closed from both ends. The columns were prepared

to have five different column ports: inlet port, three peat sample ports in the middle and outlet port. In the Figure 3, the components of the system are shown.

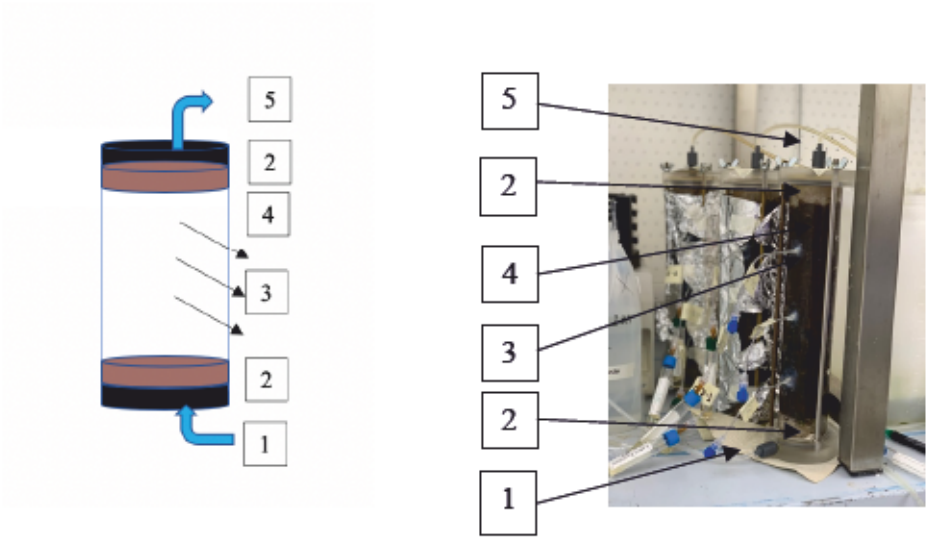

Figure 3. The column set-up used in this study: 1. Inlet 2. Quartz sand 3. Pore water samplers (Rhizon samplers) 4. Peat 5. Outlet port (Photo by: Luostarinen, 2020).

4.3 Flow-through column experiment

In this flow-through column experiment the loading and leaching scenario to be explored was to see, that whether reduced arsenic and antimony levels in inflow water lead to remobilization and redistribution of the bound contaminants in the peat columns. As in the hypothesis, this would be observable as a flattening off and traveling of the peak concentration of bound contaminant.

The first step in the flow-through column experiment was to fill the columns with inflow water with high arsenic/antimony artificial mine water. Different compositions of the artificial mine water for the loading and the leaching phase were used. The difference was mainly in the arsenic/antimony and sulfate concentrations, as those were lower in the water used for leaching part of the test. After loading with high concentration artificial water, the inflow water was changed from high arsenic/antimony to low arsenic/antimony concentrations. The more detailed information and characteristics of the artificial mine water are in the Table 2.

Table 2. Composition of artificial mine water used for loading and leaching.

	High arsenic water	**Low arsenic water**	**High antimony water**	**Low antimony water**
Sodium sulfate (g/L)	6 g/L	2 g/L	6 g/L	2 g/L
Ammoniumchloride (mg/L)	25 mg/L	25 mg/L	25 mg/L	25 mg/L
Sodiumnitrate	60 mg/L	60 mg/L	60 mg/L	60 mg/L
Sodium arsenate heptahydrate	2 mg/L	0.05 mg/L	-	-
Potassium hexahydroxoantimonate	-	-	2 mg/L	0.05 mg/L
pH	7	7	7	7

4.4 Column Setup

The flow velocities were measured in the columns in April 2020 (Table 3). Outflow was collected for about 20 h and the water volume flowed out were measured. The flow velocity was rather similar for all columns and the biggest difference was 5.04 mL/day between the highest and lowest velocity. Similar flow rate between columns was important for the accuracy of the experiment and to make results from different columns comparable.

Table 3. The measured flow velocities in the columns.

Column	Time elapsed (h)	Volume (ml)	Flow rate (mL/day)
C2	20.02	27.8	33.33
C3	20.02	27.0	32.37
C4	20.02	29.9	35.85
C5	20.02	29.1	34.89
C7	20.02	25.7	30.81
C8	20.02	27.8	33.33

A peristaltic pump model Minipuls 3 made by brand Gilson was used to pump water into the column at a pump velocity of 0.05 rpm. A pump velocity of 0.05 rpm corresponded

to a flow of approximately 30-35 mL/day (Table 3). Outflow from the column was collected in a wastewater can. A Figure of the system experiment set-up is shown in Figure 4.

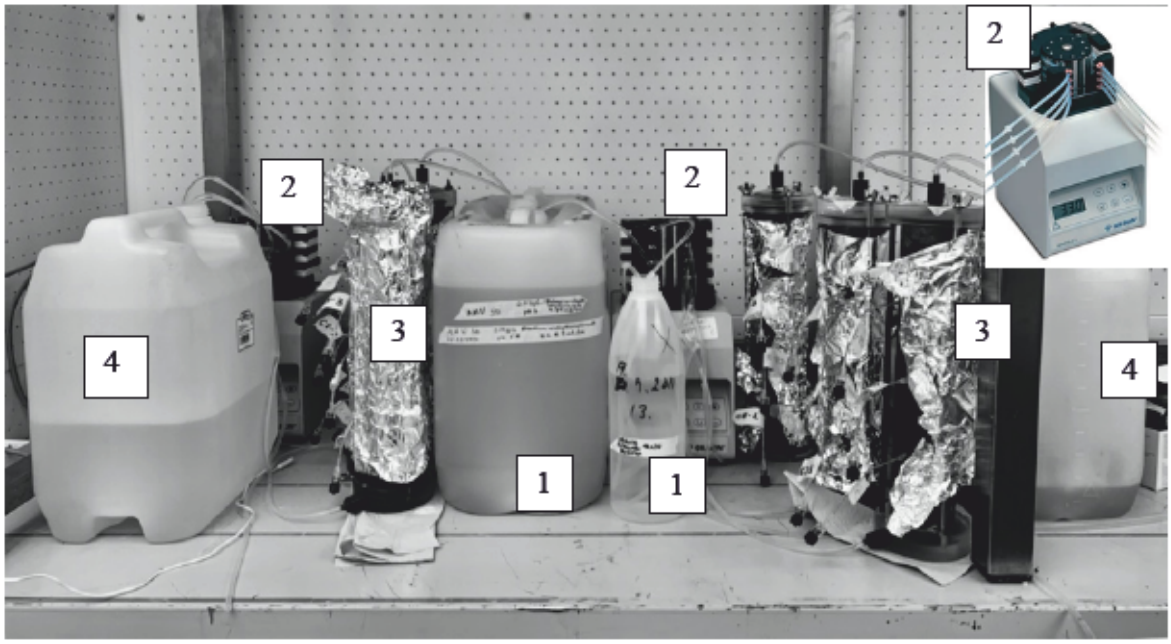

Figure 4. 1. Artificial mine water 2. Peristaltic pump 3. Column 4. Wastewater (Photo by: Luostarinen, 2020). Peristaltic pump (ManSci inc., 2020).

4.5 Sampling inflow, outflow and porewater

Water samples were taken from the inflow, outflow and porewater ports of the columns for element analysis. Columns 1, 2, 3, and 4 got their inflow water from one water container containing artificial mine water with high arsenic concentration. Columns 5, 6, 7 and 8 got their inflow from the other water container containing artificial mine water with high antimony concentration. This is why only 1 inflow sample from each inflow container was needed to cover each set of columns 1, 2, 3, 4 and columns 5, 6, 7, 8. All columns had their own outflow.

The sampling could be divided to two parts. In the first part, inlet and outlet water samples were taken and in the second part, pore water sampling was carried out. Two inlet samples of artificial mine water from each inflow container were taken (inlet sample). Inlet samples were also the only samples that were taken with a pipette. The inflow sample amount was approximately 1.5 to 2 ml. Samples of outflow water were taken by placing the outflow pipes into 2 ml tubes shown in the Figure 5. The pump velocity was

increased from 0.05 rpm to 1.5 rpm during the inlet and outlet sampling process to fasten the sampling. After the inlet and outlet sampling was finished, the pump velocity was decreased from 1.5 rpm back to 0.05 rpm. The velocity was decreased back to 0.05 rpm, because the conditions of the water flow in the peat was intended to be kept close to the natural conditions in the peatland. In treatment peatland, the water in the peat moves slowly due to the low hydraulic conductivity of peat.

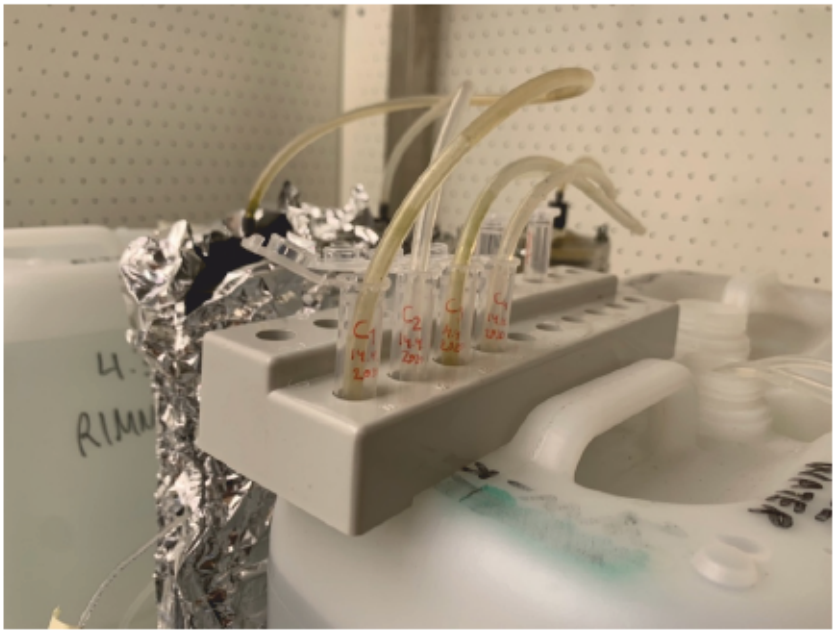

Figure 5. Outflow water sampling from columns 1, 2, 3 and 4 (Photo by: Luostarinen, 2020).

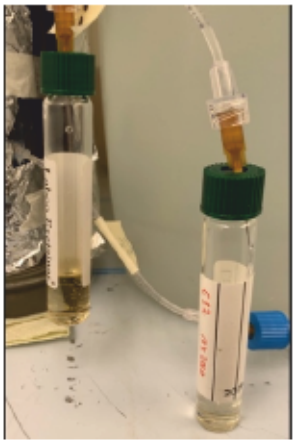

Figure 6. Porewater sampling through needles inserted into the evacuated vials (Photo by: Luostarinen 2020).

In the second part of sampling pore water samples were collected in vacuum vials through syringes attached to the Rhizon samplers (Figure 6). The size of the sample collected

varied between 4 to 5 ml. After the vials were filled between 4 to 5 ml, the vials were detached. All samples were taken at the same time from all columns as shown in the Figure 7. Depending on the amount of columns in one sampling day and how fast the evacuated vials were filling up on the sampling day, sampling process took 1 to 2 hours of time. Lastly after enough pore water sample was gathered, the needles shown in the Figure 6 were removed and the blue caps were reattached to the column ports. The vials were labeled to be able to know their port numbers in the set-up.

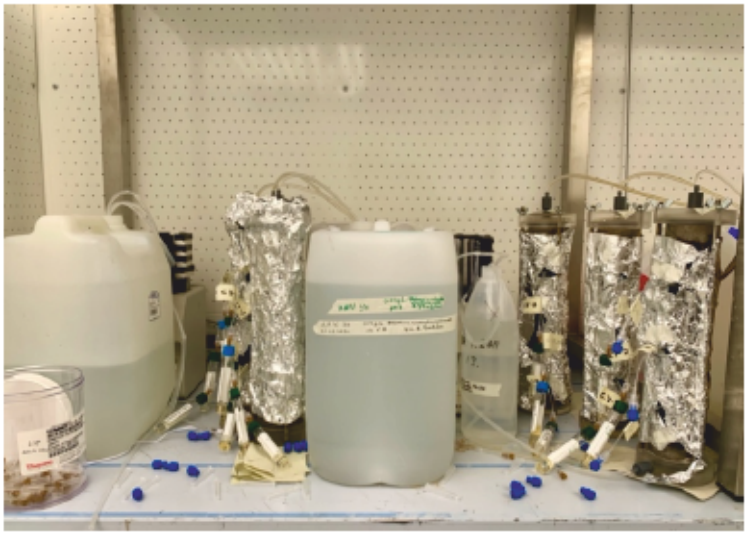

Figure 7. All three samples per column of all columns were taken at the same time (Photo by: Luostarinen 2020).

Lastly the samples in the vials were transferred to cryotubes. All samples were collected in two replicates for safety. Both samples— were filled to cryotubes to 1.5 to 2 ml per tube. If colorimetric determination of arsenic and antimony did not follow immediately both samples were stored frozen at -20°C. However, the backup samples were always stored frozen. As freezing and thawing of the samples does not affect the subsequent determination of arsenic or antimony, samples could be frozen and collected to analyze them in bigger batches.

4.6 Sampling schedule

The flow through column experiment had 14 sampling days (Table 4). The sampling schedule depended on the exposure time of each column in the experiment. Columns 1 and 6 had the least exposure time because they were sacrificed on April 20th (see 4.11) and were thus sampled only twice. Column 5 had only two sample days, because the

column was not working correctly until 4.5.2020. Columns 4 and 8 were under intensive monitoring as they were the last columns to be sacrificed and samples were taken from them on 14 different days. As columns 4 and 8 had the longest exposure time in the leaching experiment, they provide the most consistent measurement data in terms of number of sampling timepoints. Because of this, additional focus will be given to the assessment of these two columns in results and discussion chapter.

Table 4. Sampling days. C stands for column and x for a sample.

Sampling day	C1	C2	C3	C4	C5	C6	C7	C8
1. (14.4.2020)	X	X	X	X		X	X	X
2. (17.4.2020)	X	X	X	X		X	X	X
3. (22.4.2020)		X	X	X			X	X
4. (24.4.2020)		X	X	X			X	X
5. (28.4.2020)		X	X	X			X	X
6. (4.5.2020)		X		X	X			X
7. (8.5.2020)		X		X	X			X
8. (11.5.2020)				X				X
9. (13.5.2020)				X				X
10. (15.5.2020)				X				X
11. (18.5.2020)				X				X
12. (26.5.2020)				X				X
13. (29.5.2020)				X				X
14. (1.6.2020)				X				X
Sum of sampling days	2	7	5	14	3	2	5	14

4.7 Colorimetric determination of antimony

Antimony concentration was determined in inflow, outflow and porewater samples taken from the columns. The determination of antimony was based on the method developed in Australia. The colometric method is based on the development of the yellow potassium iodoantimonite complex and the measurement of its absorbance at 425 nm (Tighe et al. 2018). The determination of antimony concentration could be done immediately after the samples were taken or after melting frozen samples (see 4.5). Frozen samples were allowed to thaw completely before starting the analysis.

The determination of antimony was divided into preparation of 8 calibration standards, reagents and doing the analysis on the microplate shown in the Figure 8. Calibration standards with known antimony concentrations were prepared from stock solution of antimony. 10 mM stock solutions were diluted 1:10 to obtain secondary stock solutions with a concentration of 1 mM. Calibration standards ranging in antimony concentration from 0 to 30 µM were prepared directly in the 96-well plates using this secondary stock as shown in the Table 5.

Table 5. The composition of 8 calibration standards for antimony color determination.

Antimony concentration (µM)	**Volume of 1 mM antimony stock (µl)**	**Volume MQ water (µl)**
0	0	100
1	1	99
4	4	96
7	7	93
10	10	90
15	15	85
20	20	80
30	30	70

In the second part, the Potassium iodide (KI) reagent was prepared. Potassium iodide (KI) reagent was prepared by dissolving 1 g ascorbic acid and 5.6 g potassium iodide in MQ to total volume of 50 ml.

For the analysis the standards and all samples were pipetted to the microplate in triplicates. For the analysis of triplicate samples, 20 µl concentrated H_2SO_4 was added to 100 µl sample or standard and mixed by pipetting up and down several times. Lastly, KI reagent was added to all samples to final volume of 100 µl and mixed by pipetting.

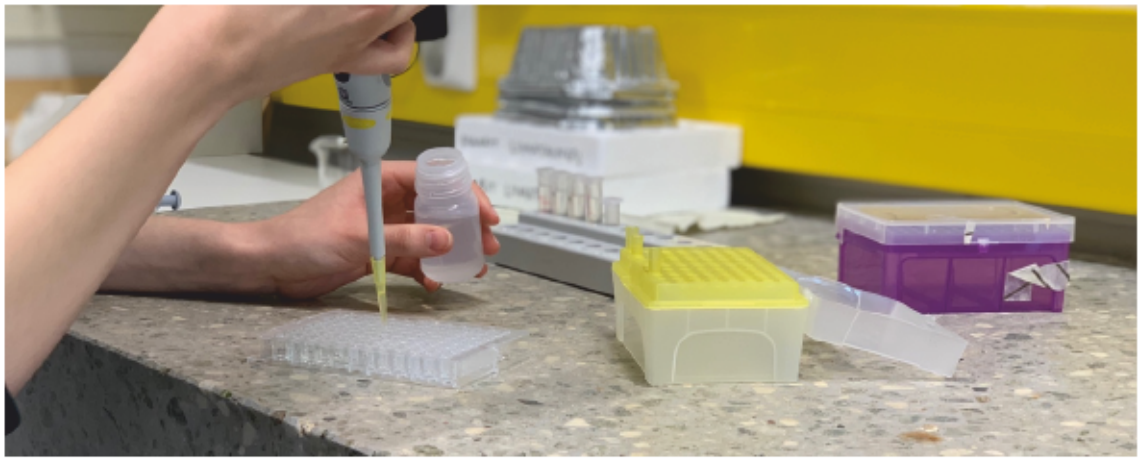

Figure 8. Microplate (Photo by: Luostarinen 2020).

The samples were allowed to react at least for 5 minutes for the reaction to complete. Lastly, absorbance was read at 425 nm with the absorbance plate reader Spectro star nano by BMG labtech shown in the Figure 9.

Figure 9. Absorbance plate reader used for reading absorbance. The concentration of pore water can be calculated from the known absorbance. (Photo by: Luostarinen 2020).

4.8 Calculation of antimony concentration

The antimony concentrations based on the absorbance readings were calculated after the analysis. First, the standards average blank reading was subtracted from other readings. Second, a calibration curve was drawn of the standards with a linear trendline. Lastly the total concentration of antimony in samples was calculated by dividing the obtained absorbance values by the slope of the calibration curve.

4.9 Colorimetric determination of arsenic

Arsenic concentration was determined in inflow, outflow and porewater samples taken from the columns. The determination of arsenic was based on the method developed by Johnson and Pilson (Johnson & Pilson, 1972). The determination of arsenic concentration was followed after the samples for the determination was taken from the flow-through column experiment. The determination of arsenic concentration could be done immediately after sampling or after melting the frozen samples (see 4.5). Frozen samples were allowed to thaw completely before starting the analysis.

The determination of arsenic was divided into preparation of 8 calibration standards, reagents and doing the analysis on the microplate. Calibration standards with known arsenic concentrations were prepared from stock solutions of arsenate and phosphate. 10 mM stock solutions were diluted 1:10 to obtain secondary stock solutions with a concentration of 1 mM. Calibration standards ranging in arsenate concentration from 0 to 30 µM were prepared using these secondary stocks as shown in the Table 6. The standards were prepared in Eppendorf tubes with total volume of 1 ml for a single standard.

Table 6. The composition of 8 calibration standards for arsenic color determination.

Arsenate concentration (µM)	**Volume of 1 mM arsenate stock (µl)**	**Volume of 1 mM phosphate stock (µl)**	**Volume MQ water (µl)**
0	0	2	998
1	1	2	997
3	3	2	995
5	5	2	993
7	7	2	991
10	10	2	988
20	20	2	878
30	30	2	868

After the standards were prepared, the second step was to prepare three reagents. The three reagents were oxidizing solution, reducing solution and color reagent.
The oxidizing solution had 2 mM KIO_3, which was prepared by dissolving 0.0425 g potassium iodate in MQ containing 2 % HCl to total volume of 100 ml.

The reducing solution was prepared with mixing 14 % $Na_2S_2O_5$, 1.4 % $Na_2S_2O_3$ and 10 % H_2SO_4 with MQ water. The three solutions were mixed in ratios of 2:2:1 by volume. The color reagent was prepared from four reagents: 10.8 % ascorbic acid ($C_6H_8O_6$), 3 % ammonium molybdate ($(NH_4)_6Mo_7O_{24}$ x 4 H_2O), 0.56 % antimony potassium tartrate ($C_8H_4K_2O_{12}Sb_2$. 3 H_2O) and 13.98 % H_2SO_4. The ratio of the reagents was 2:2:1:5.

The analysis procedure of arsenic was first to acidify all samples with 6N HCL. 10 µl was added per 1 ml standard and sample. In arsenic analysis all three samples were treated differently. The samples were treated by the following procedure: i) 200 µl sample was treated with 25 µl oxidizing reagent, ii) 200 µl sample was treated with 25 µl mixed reducing agent and iii) 200 µl sample was treated with 25 µl 2 % HCl. These three different reactions oxidizing, reducing and HCl were done once per each sample to get information about sample's total arsenic, arsenate and phosphate concentrations. As three different reactions had to prepared for each sample, samples were not analyzed in triplicate because it would have resulted in a very high pipetting effort. The samples were allowed to react for 10 minutes. After this 25 µl mixed color reagent was added, the standards and samples were mixed well and left to react for 10 minutes. After reaction the 96-well-plate's absorbance was read at 880 nm wavelength.

4.10 Calculation of arsenic concentration

The total arsenic concentration based on the absorbance readings were calculated after the analysis. The idea behind the calculations of concentration was that only phosphate can be detected with the reducing reagent , while phosphate + arsenate can be detected with the HCl and finally phosphate + arsenate + arsenite can be detected with the oxidizing solution.

First, the standards average blank reading was subtracted from oxidizing, reducing and HCl readings of the same treatment. Secondly the total arsenic amount was calculated by subtracting the values of the reducing treatment (i.e. absorbance caused by phosphate only) from the oxidizing treatment (i.e. absorbance caused by phosphate + arsenite + arsenate). Next the total amount of arsenate was calculated by subtracting the values of the reducing treatment (i.e. absorbance caused by phosphate) from the values of the HCl treatment (i.e. absorbance caused by phosphate + arsenate). This was followed by forming a calibration curve of the standards with a linear trendline. Lastly the total concentration

of arsenate and arsenic in samples was calculated with the equations obtained from the calibration curve.

In cases where the concentration amounts were negative, the amount was replaced with zero. In the results chapter, only results for arsenate are shown even though both arsenate and arsenite were measured in the samples. The reason for this is that during the calculations of total arsenite concentration, it was found out that there is no arsenite in the samples.

4.11 Destruction of the columns

Columns were sacrificed to extract peat for analysis of the concentration of different contaminants. Before destruction, the water pump of the respective column was taken off, so that the water would drain out of the peat and the peat would be more easier to be removed from the column and cut into sections. Destruction of the column was done 2-5 days after taking the pump off the column. The timeline and the order for the destruction of the columns is shown in the Table 7.

Table 7. The timeline and the order for the destruction of the columns.

DATE	OPERATION
20th April 2020	The columns C1 and C6 were taken off the pump
20th April 2020	The inflow water was changed from high As / Sb to low As / Sb for the remaining columns
22nd April 2020	Destruction of the columns C1 and C6
30th April 2020	The columns C3 and C7 were taken off the pump
5th May 2020	Destruction of the columns C3 and C7
8th May 2020	The columns C2 and C5 were taken off the pump
12th May	Destruction of the columns C2 and C5
1st June 2020	The columns C4 and C8 were taken off the pump
4th June 2020	Destruction of the columns C4 and C8

The deconstruction of the columns was divided in to 4 parts. At each part two columns were sacrificed: 1 x arsenic column and 1 x antimony column. In the deconstruction operation, 25 cm long peat column shown in the Figure 10 was opened up.

The peat sample analysis included eight columns and two reference peat samples. The columns were divided into 3-centimeter parts. Columns 3 and 7 were divided into seven different parts, columns 1, 6 and 8 were divided into ten different parts, column 2, 4 and 5 to nine different parts. Depending on the amount of moisture peat had, it became longer than 25 cm when the peat was pushed out from the column. Due to this, the number of 3 cm sections varies between the columns.

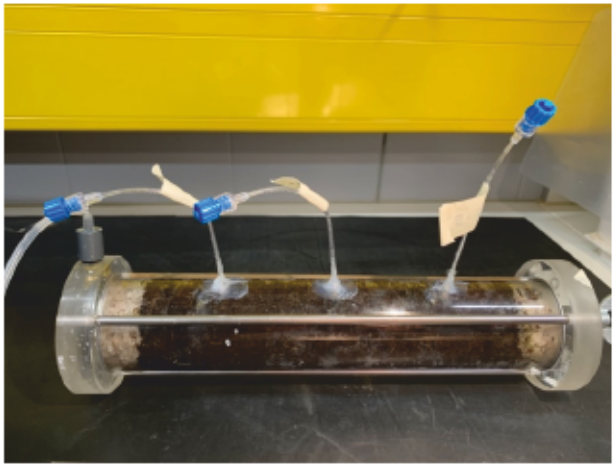

Figure 10. A peat column immediately before dismantling (Photo by: Luostarinen, 2020).

4.12 Sampling and analysis of the peat

Shown in Figure 11 is a destroyed column without tubes and column top and bottom. Each 3 cm section of peat (Figure 12) was put separately in an individual plastic bag as shown in the Figure 13, stored in 4 °C temperature until the peat samples were sent for analysis of arsenic and antimony concentrations to Eurofins Laboratory.

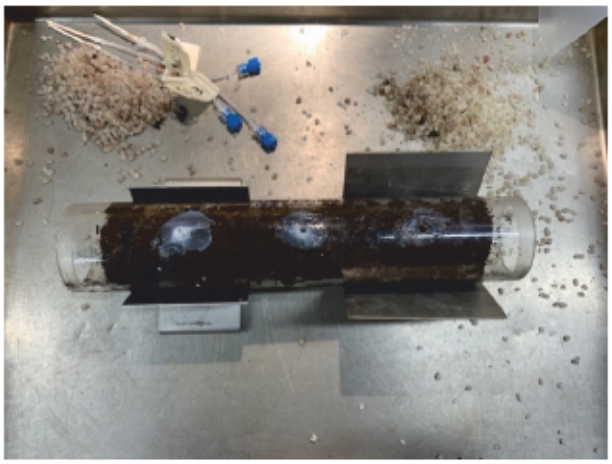

Figure 11. Destroyed column (Photo by: Luostarinen, 2020).

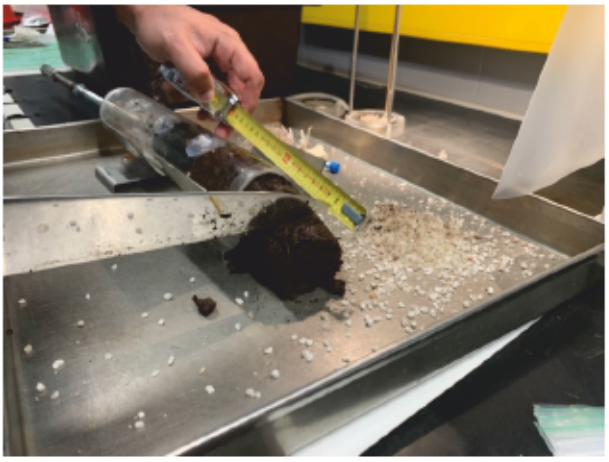

Figure 12. The peat was cut into 3 cm samples (Photo by: Luostarinen, 2020).

Figure 13. The 3 cm sections of peat separately in plastic bags (Photo by: Luostarinen, 2020).

4.13 Measurement of concentrations in peat

The peat sample analysis was carried out at Eurofins following the applicable standards of the International Organization for Standardization (ISO). Methodological standards are used to study, monitor, and control the state of the environment for consistency of the measurements. They play a key role, especially in the implementation of EU directives. The chosen method of analysis was based on ICP-MS following SFS-EN ISO 17294-2: 2016 for arsenic, antimony, manganese and iron. SFS-EN ISO 17294-2: 2016 is a standard for water quality (Syke, 2019).

5 RESULTS AND DISCUSSION

Two different measurement methods were used in order to obtain more reliable data for conclusions about the removal and leaching of contaminants in the peat columns. Columns 4 and 8 had the longest exposure time in the leaching experiment and most consistent measurement data by the number of sampling timepoints. Because of this, additional focus will be given to the assessment of these two columns. Leaching and contaminant mobilization in peat is a process in nature and due to the time span, the process perspective remained short. The flow-through column experiment was done with 8 columns, in one laboratory and for longest of 48 days. Short experiment time may not show similar results as an experiment that would last for longer, for example for a year.

5.1 Effect of inflow water concentration on antimony concentration in porewater

Analysis of inflow, outflow and porewater showed that antimony starts leaching from the peat as the concentration in the inflow water decreases. Higher antimony concentrations can be seen in all ports and especially the outflow as the exposure period to low concentration inflow water continues.

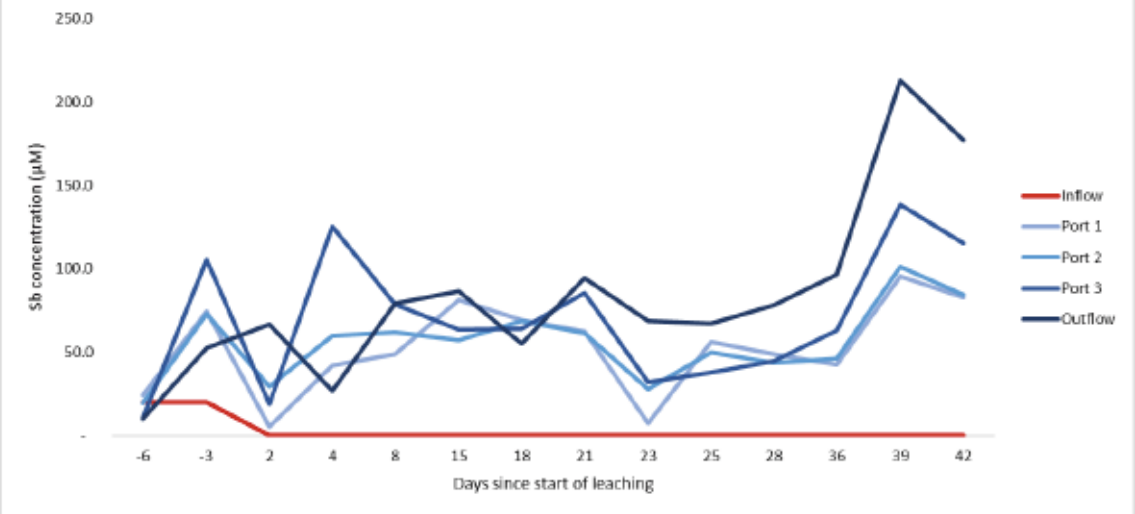

Figure 17. Antimony concentrations in inflow, outflow and porewater collected from **column 8** over the course of the experiment. Day=0 represent the time when inflow water was changed from high antimony concentration (20.0 µM) to low concentration (0.5 mg/l

~ 1.5 µM). Port 1, 2 and 3 represent porewater collected at 6 cm, 12.5 cm and 18.5 cm from the inlet.

Figure 17 shows that the antimony concentration for column 8 in the outflow water increases steadily over the course of the experiment. A similar pattern of increased antimony concentration, especially towards the end of the experiment period (Day 25-42), can be observed for the antimony concentration measured in the porewater from ports 1, 2 and 3. Between day 2 – 21 the sampling timepoints with the highest antimony concentration varies between ports 1, 2, 3 and the outflow, whereas after day 21 the highest antimony concentration is always measured in the outflow water. Table 8 shows that after day 36 the average amount of antimony measured from all ports and outflow water was substantially higher than the average for the entire duration of the experiment.

Table 8. Average antimony concentrations (µM) for Port 1, 2, 3 and outflow for **column 8**. Average = average of all sampling timepoints for the period.

	Average Sb concentration (µM)		Standard Deviation		n (# of measurements)	
	Total Experiment	Day 36-42	Total Experiment	Day 36-42	Total Experiment	Day 36-42
Port 1	52.9	73.5	26.4	22.6	14.0	3.0
Port 2	56.0	77.3	21.6	23.1	14.0	3.0
Port 3	70.2	105.8	38.6	31.6	14.0	3.0
Outflow	83.7	162.2	51.4	48.5	14.0	3.0

These findings (Figure 17 and Table 8) indicate that as inflow concentration is decreased from 20 µM to ~1.5 µM at day 0, the longer the exposure time to low concentration inflow water is, the more antimony was leached.

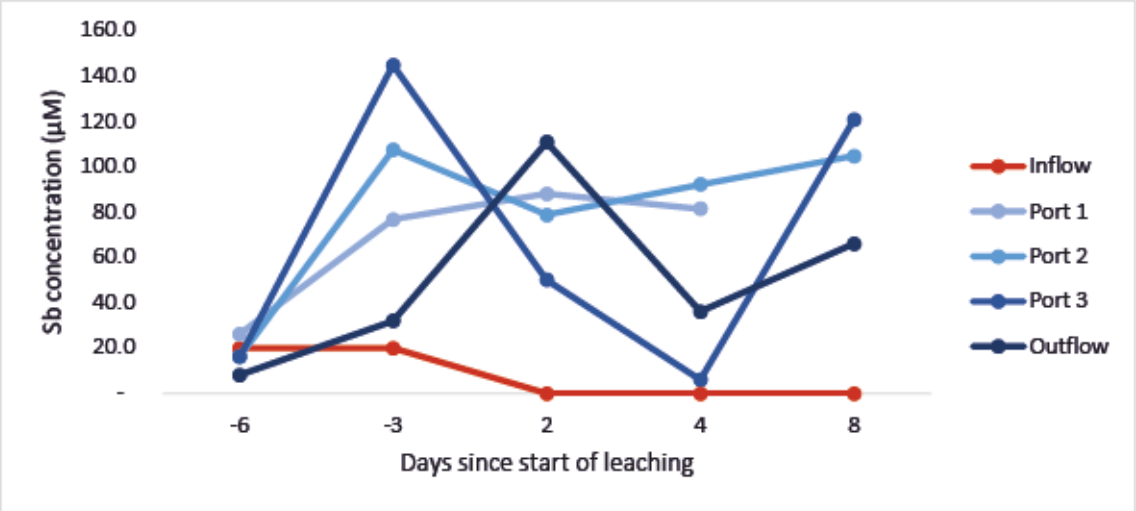

Figure 18. Antimony concentrations in inflow, outflow and porewater collected from **column 7** over the course of the experiment. Day=0 represent the time when inflow water was changed from high antimony concentration (20.0 µM) to low concentration (0.0 µM). Port 1, 2 and 3 represent porewater collected at 6 cm, 12.5 cm and 18.5 cm from the inlet.

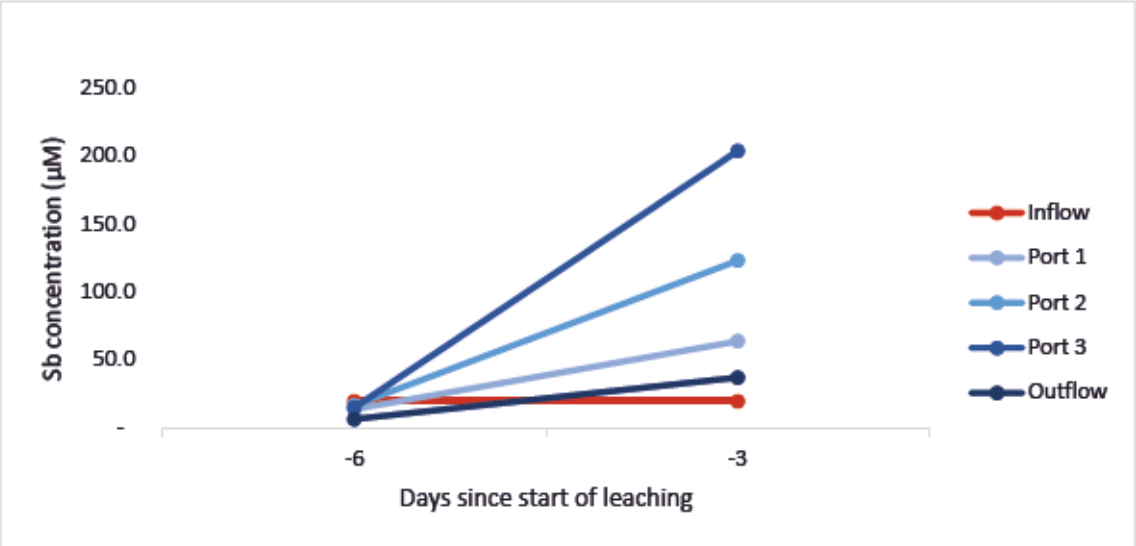

Figure 19. Antimony concentrations in inflow, outflow and porewater collected from **column 6** over the course of the experiment. Day=0 represent the time when inflow water was changed from high antimony concentration (20.0 µM) to low concentration (0.0 µM). Port 1, 2 and 3 represent porewater collected at 6 cm, 12.5 cm and 18.5 cm from the inlet.

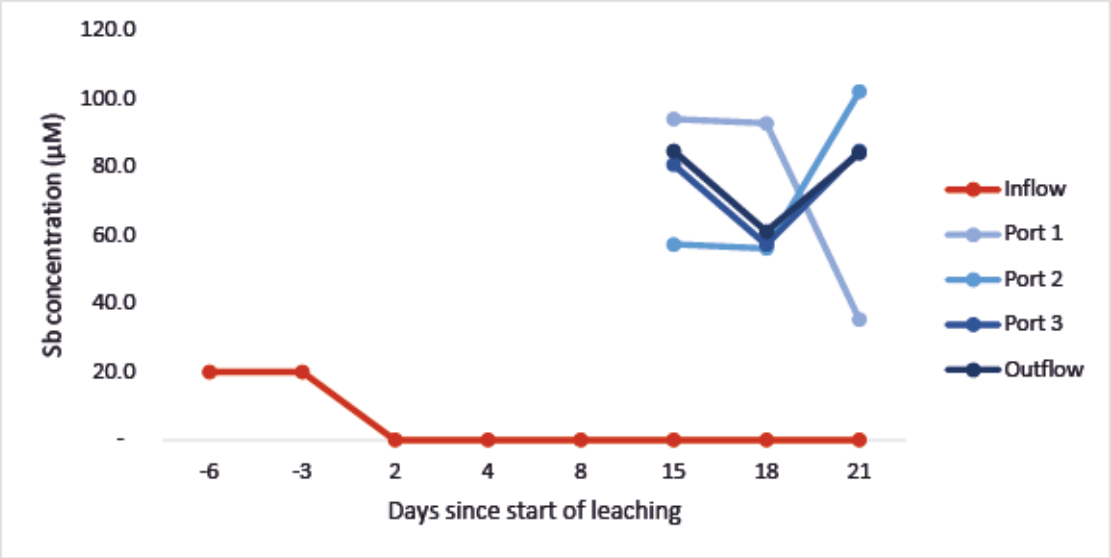

Figure 20. Antimony concentrations in inflow, outflow and porewater collected from **column 5** over the course of the experiment. Day = 0 represent the time when inflow water was changed from high antimony concentration (20.0 µM) to low concentration (0.0 µM). Port 1, 2 and 3 represent porewater collected at 6 cm, 12.5 cm and 18.5 cm from the inlet.

A similar pattern of increasing antimony concentration as a derivative of exposure time since the inflow water concentration was lowered to 0 µM can be partially observed in columns 7 and 5 shown in the Figures 18 and 20, respectively. Even though both columns have less sampling timepoints (dates) than column 8, both columns show a higher antimony concentration in outflow on measurement days after day 0 (=start of leaching). (Column 5 all sampling timepoints average before day zero 53.4 µM, after day zero 75.8 µM. Column 7 all sampling timepoints average before day zero 60.2 µM in outflow, after day zero 101.0 µM). Even though columns 5 and 7 do not provide sufficient standalone results due to the lower exposure time to low concentration inflow water and less sampling timepoints, they do provide support to the findings in column 8 (column 7 destroyed at day 8 and column 5 destroyed at day 21). Column 6 shown in Figure 19 was destroyed at day 0 and thus does not provide sufficient measurement data to make conclusions based on it.

5.2 Effect of inflow concentration on retention of antimony in peat

Analysis of antimony concentration in the peat showed that antimony starts leaching from the peat over time as the antimony concentration in the inflow water is decreased.

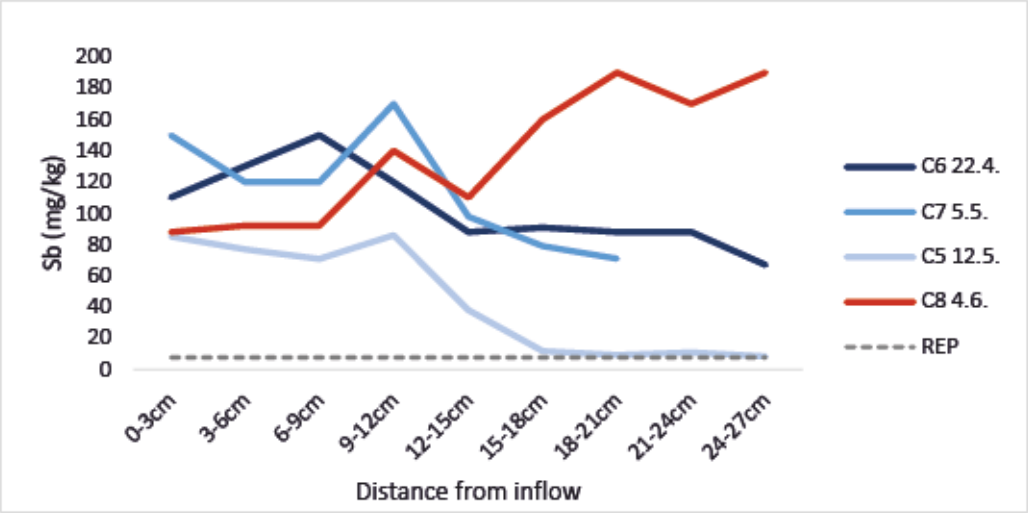

Figure 21. Antimony concentration in peat measured by distance to inflow compared by exposure time. Inflow water was changed from high antimony concentration (20.0 µM) to low concentration (0.0 µM) on 22.4. (day 0 in colorimetric determination charts). REP shows the concentration of reference peat taken from Kittilä. The date after the column number represents the date on which the column was sacrificed.

The Figure 21 shows that the antimony accumulation in peat moves further away from the inflow point as exposure time to low antimony water is increased. Column 8 which had the longest exposure time depicts a steady increase in the antimony the further (18-27 cm) it is measured from the inflow point. Column 8 shows that not only has the highest concentration point of antimony moved further away from the inflow point, but that the absolute antimony concentration for distances > 15 cm from the inflow point has doubled to an average (four sampling timepoints for 15-27 cm) of 177.5 mg/kg compared to column 6 average of 83.5 mg/kg which had the shortest exposure time.

Columns 5 and 7 which had a similar exposure time to one another, but less than column 8, shows that antimony concentration is the highest in the middle part of the column (9-15 cm from inflow). They both also show a decrease in the antimony concentration at higher distances to the inflow point. Column 6 which had the shortest exposure time shows the highest concentration closest to the inflow (3-9 cm). The comparison of these four columns suggest that there is a clear pattern in which the highest antimony concentration level moves further away from the inflow point as the exposure time to the low concentration inflow water increases.

5.3 Conclusions on antimony leaching behavior based on combined results from peat and water

Both measurements in peat and porewater show similar results in the behavior of antimony in leaching. Both data sets depict that as exposure time to the low concentration inflow water increases, the peak antimony concentration in peat moves further away from the inflow point. This can be concluded both from the increasing antimony concentration in the outflow water and the increase in distance from the inflow for high antimony concentration in peat.

The results prove that for both peat and water, as the exposure time increased not only did the point with highest antimony concentration in water move further away from the inflow point, but also that the absolute amount of antimony leached increased. For column 8, which had the longest exposure time, antimony concentrations measured in peat for distances > 15 cm away from the inflow point averaged at 177.5 mg/kg, which is over 3 times higher than the average 52.5 mg/kg for all the other columns. These findings provide support to the hypothesis of this study that *Reduced arsenic/antimony level in inflow water will lead to remobilization and redistribution of the bound contaminants in the peat columns which will be observable as a flattening off and traveling of the peak concentration of bound contaminant.*

5.4 Effect of inflow concentration on the arsenate concentration in porewater over time

In column 4 the outflow concentration of arsenate was in the beginning of the experiment 6 µM. Outflow concentration of arsenate varied between 2 – 20 µM during the whole experiment. Outflow concentration of arsenate was the same as inflow concentration 7 µM on one day after the leaching started. Outflow concentration of arsenate reached to 20 µM 15 days after the leaching started. Arsenate concentration 20 µM was the same concentration that was the concentration of artificial mine water used for loading. Outflow concentration reached loading mine water concentration only once during the experiment. Most of the sampling times the outflow concentration was the highest. However, 8, 21 and 36 days after the leaching was started the highest concentration was measured from ports. On day 8 from leaching it was measured in port 2 which was 6 cm

from inlet and on days 21 and 36 it was measured in port 1 which was 12.5 cm from the inlet. At the end of the experiment the lowest concentrations were near inlet and the highest concentrations in port 3 and outlet.

Arsenate starts leaching from the peat as its concentration in the inflow water decreases (Figure 22). After the inflow water is changed to low concentration, the average arsenate concentration measured from ports 1, 2, 3 and outflow increases on days 8-21 to an average of 11.1 µM (average for all ports and outflow). After day 21 the arsenate concentration decreases to an average of 6.2 µM (average for all ports and outflow), which is lower than the average concentration 8.3 µM before day zero.

In results only arsenate concentration was used instead of total arsenic. This was evident due to concentration measurements, in which in most cases total arsenic and arsenate concentrations were very similar. In these measurements, arsenate was the dominating arsenate species.

Arsenate concentration was spread more evenly than antimony over time and there is no single sampling timepoint which has the highest concentration unlike antimony where the outflow concentration was clearly higher than the ports towards the end of the experiment.

A similar pattern as in column 4 can be seen in columns 3 (Figure 23) and 2 (Figure 24) as the highest concentrations were measured in the outflow on day 8 – 15 after the onset of leaching. Column 2 average (all sampling timepoints) arsenate concentration before day zero was 10.8 µM, and after day zero it was 19.1 µM. Column 3 average arsenate concentration before day zero was 10.3 µM, and after day zero it was 38 µM. Even though columns 2 and 3 do not provide sufficient standalone results due to short exposure time to low concentrate water and small amount of sampling timepoints, combined with the findings of column 4 they do support the evidence that arsenate concentration in outflow increased after inflow water is changed to low concentration. Column 1 (shown in the Figure 25) was destroyed on day 0 and thus does not provide sufficient evidence for conclusions.

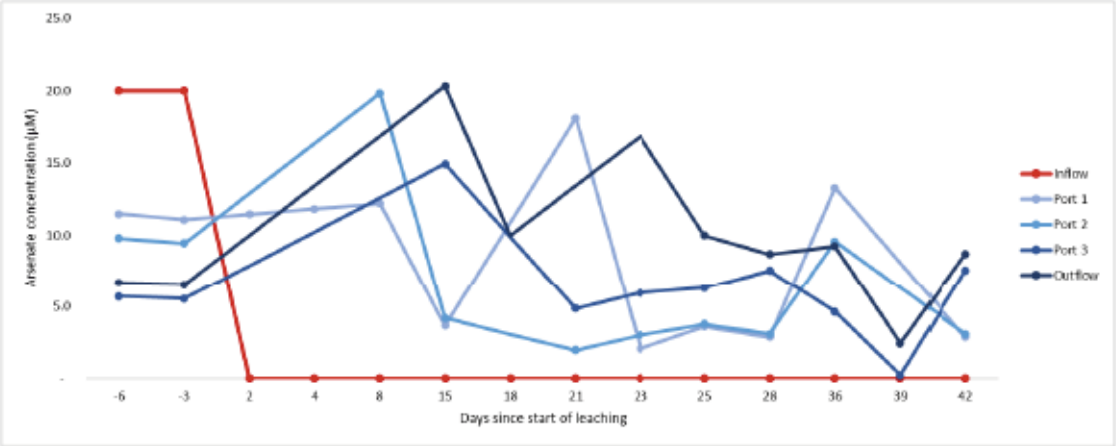

Figure 22. Arsenate concentrations in inflow, outflow and porewater collected from **column 4** over the course of the experiment. Day = 0 represent the time when inflow water was changed from high arsenic concentration (20.0 µM) to low concentration (~1.5 µM). Port 1, 2 and 3 represent porewater collected at 6 cm, 12.5 cm and 18.5 cm from the inlet.

The Figure 22 shows that the arsenate concentration measured in the porewater and outflow for column 4 over time is much less concise than the measurement results for antimony in column 8.

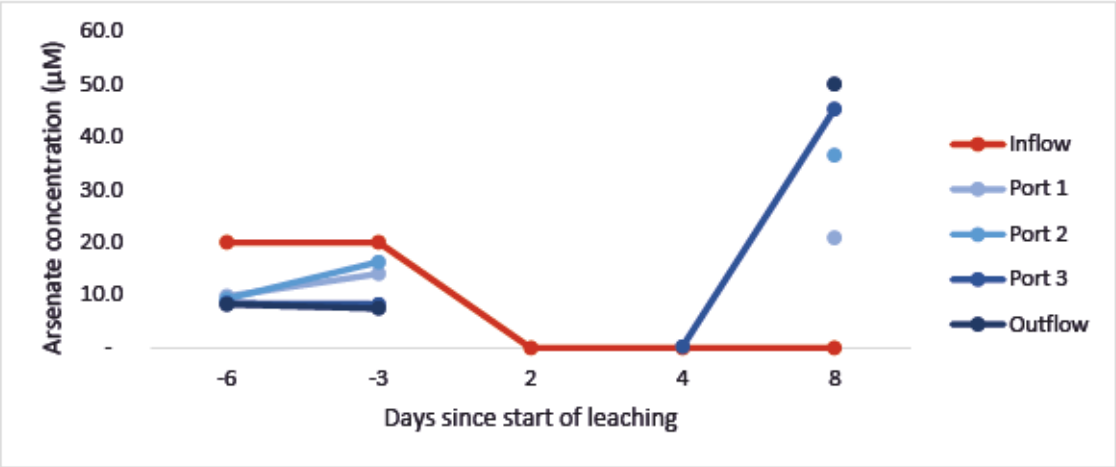

Figure 23. Arsenate concentrations in inflow, outflow and porewater collected from **column 3** over the course of the experiment. Day = 0 represent the time when inflow water was changed from high arsenic concentration (20.0 µM) to low concentration (0.0 µM). Port 1, 2 and 3 represent porewater collected at 6 cm, 12.5 cm and 18.5 cm from the inlet.

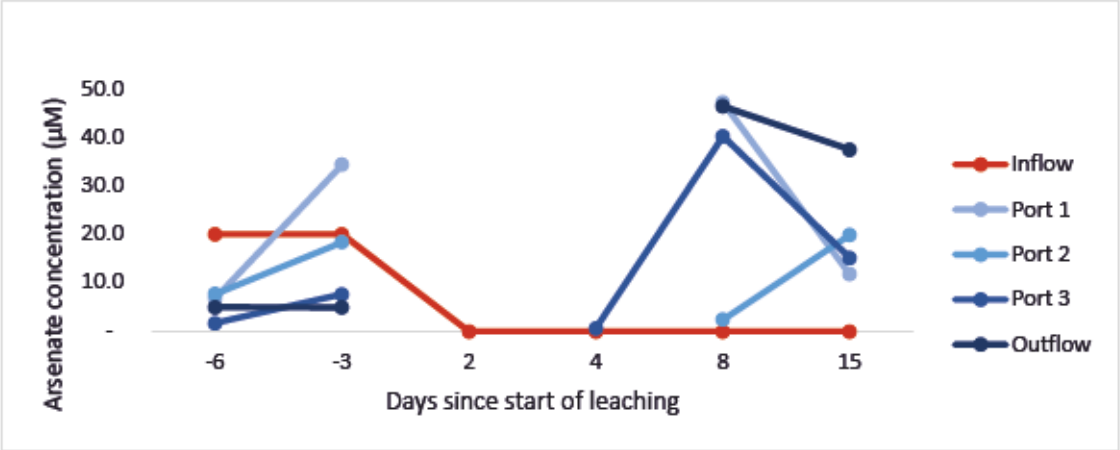

Figure 24. Arsenate concentrations in inflow, outflow and porewater collected from **column 2** over the course of the experiment. Day = 0 represent the time when inflow water was changed from high arsenic concentration (20.0 µM) to low concentration (0.0 µM). Port 1, 2 and 3 represent porewater collected at 6 cm, 12.5 cm and 18.5 cm from the inlet.

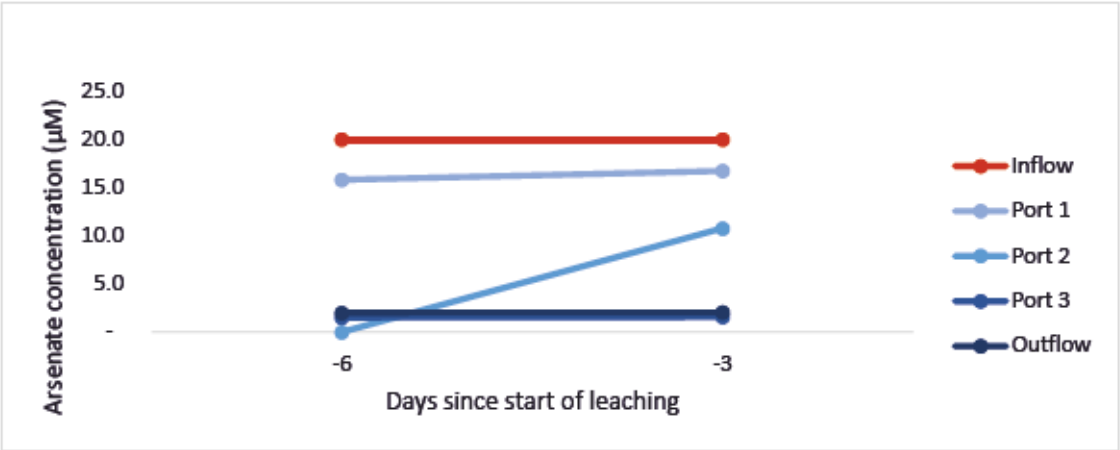

Figure 25. Arsenate concentrations in inflow, outflow and porewater collected from **column 1** over the course of the experiment. Day = 0 represent the time when inflow water was changed from high arsenic concentration centration (20.0 µM) to low concentration (0.0 µM). Port 1, 2 and 3 represent porewater collected at 6 cm, 12.5 cm and 18.5 cm from the inlet.

5.5 Effect of lowering inflow concentration on the retention of arsenic in peat

Analysis of arsenic concentration in peat showed that arsenic starts leaching from the peat over time as the arsenate concentration in the inflow water is decreased. Arsenate

concentration is high closer to the inflow for column 1 which was analyzed the earliest (lowest exposure time) and especially high further away from the inflow for column 4 which was analyzed the latest (longest exposure time).

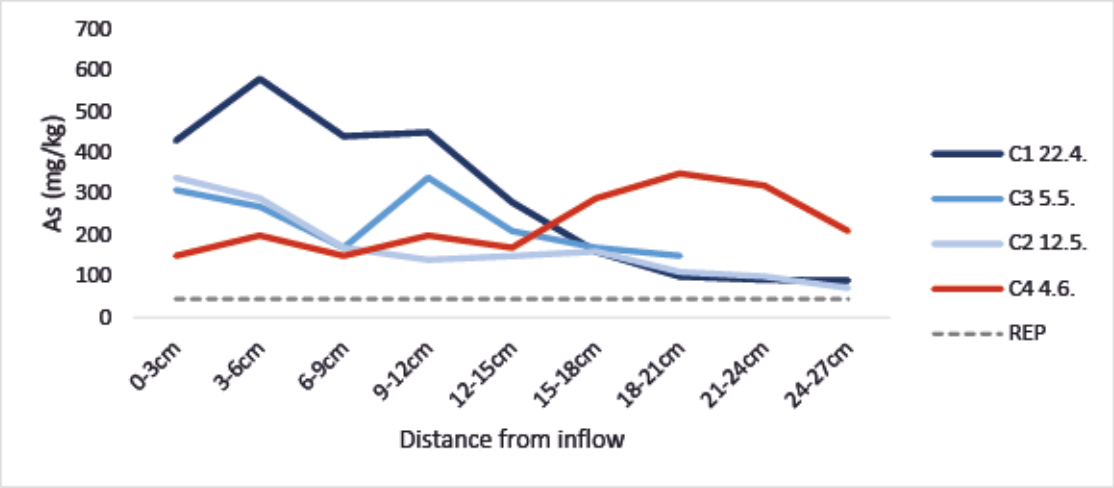

Figure 26. Arsenic concentration in peat measured by distance to inflow compared by exposure time. C1, C2, C3 and C4 are columns 1, 2, 3 and 4 from the experiment. The date after column indicates the date in which it was terminated. Inflow water was changed from high arsenic concentration (20.0 µM) to low concentration (0.0 µM) on 22.4. (day 0 in colorimetric determination charts). REP shows the amount of arsenate (mg/kg) in the reference peat taken from Kittilä. The date after the column number represents the date on which the column was sacrificed.

The Figure 26 shows that the highest arsenate concentration moves further away from the inflow as a result of longer exposure time to the low concentration inflow water. Column 1 which had the least exposure time to the low concentration inflow water shows high concentration (average of 490 mg/kg) of arsenate close to the inflow (3 - 12 cm) and over 4 times lower (average of 94 mg/kg) concentration further away from the inflow (18 - 27 cm). Columns 3 and 2 which had a similar exposure time to one another (longer than column 1 and shorter than column 4) shows that the arsenate concentration is spread more evenly compared to the distance from inflow. Even though the concentration is more evenly spread it is also visible that the first half (3-15 cm) has a higher concentration (average of 247.5 mg/kg for Column 3, average of 187.5 mg/kg for column 2) than the latter half (15-27 cm) (average of 110.5 mg/kg for column 3, average of 160 mg/kg for column 2).

Column 4 which had the highest exposure time arsenate to the low concentration inflow water shows that the highest concentration of has moved further away from the inflow (15-24 cm). Column 4 also has the highest absolute concentration of arsenate on the sampling timepoints further than 15cm from the inflow point. The highest arsenate concentration point (350 mg/kg) for column 4 is at 18-21 cm from the inflow point and after this point the arsenate concentration decreases slightly towards the end, but it does not reach the before 15 cm levels of arsenate concentration.

5.6 Conclusions on arsenic leaching behavior based on combined results from peat and water

The results obtained from the analysis of peat and water do not provide concise results on the leaching of arsenic. Even though the exposure time to the low concentration inflow water was the same for both measurement methods the colorimetric determination shows a more even split of the arsenate concentration over time between the measurement ports and outflow, it also shows that the highest concentrations were measured on days 8-15. Unlike the concentration in porewater, the peak arsenic concentration in peat moves steadily further away from the inflow point as exposure time increases.

Even though the results obtained from the analysis of peat and water, when considered individually, do not provide concise results on the spread of arsenic concentration as compared to exposure time or distance from the inflow point, both measurement together do provide support to the hypothesis of this study that *Reduced arsenic/antimony level in inflow water will lead to remobilization and redistribution of the bound contaminants in the peat columns which will be observable as a flattening off and traveling of the peak concentration of bound contaminant.*

In addition, measurement of arsenic in peat shows that the highest concentration for column 4 is 15-21 cm from the inflow point and when moving still further away from the inflow to 24-27 cm the concentration decreases. This possibly suggest that if the exposure time was still further increased the highest arsenic concentration point would possibly still move further away from the inflow point. There is a high correlation between the arsenic concentration movement as a result of longer exposure time so I would consider this to be a possibility. Taking into consideration the limitations of this research it cannot

of course be concluded that this would be the case, but it would be a possible opportunity to research the impact of an even longer exposure time to low concentration inflow water.

5.7 Discussion

In their study published in 2019, Khan et al. studied the contaminant removal and leaching in batch incubations with unmodified natural peat. Their research showed that unmodified peat has a good capacity to remove arsenic and antimony from mining-influenced waters, but also that the dilution of mining-influenced waters leads to contaminant leaching. In their study (Khan et al. 2019), it was noted that once the tested mining-influenced water was diluted there was a major effect on removal/leaching of the contaminants. They concluded that contaminants are not actually absorbed permanently to peat, but more likely chemically or physically bound and therefore easily leachable if the chemical balance changes. The findings of Khan et al. (2019) are supported by the findings of this study as the results from batch incubation experiments in their study were corroborated by column experiments in this study. Once the chemical composition of the inflow water was changed from high concentration to diluted low concentration inflow water, it was evident that both antimony and arsenic started leaching. These results were evident from water and peat analysis for both antimony and arsenic. For both antimony and arsenic it was visible that as the exposure time to the diluted inflow water increased, the highest concentration point in peat moved further away from the inflow point. For antimony it was also visible that as the exposure time increased it was not only the highest concentration point which moved further away from the inflow point but that also the absolute amount of antimony leached increased.

Palmer et al. (2015) have also studied the efficient removal of arsenic, antimony and nickel from mine wastewaters. The study concluded that contaminants like arsenic, antimony and nickel can be efficiently retained in peatlands which indicated that peatlands are in fact well suited for the efficient purification of mining wastewaters. However they also found that the leaching of contaminants is to be anticipated in situations where clean natural waters mix with mine waters e.g. during snowmelt or after mine closure and that especially easily mobilized (i.e., loosely-bound) fractions of arsenic, antimony, and nickel are likely to leach from the treatment peatlands.

The findings of Palmer et al. (2015) was partially replicated in this study under laboratory conditions. The findings of this study support the conclusions made by them. This research showed that once the inflow water was diluted to low concentration (comparable to Palmer et al. study natural waters) the leaching of both arsenic and antimony materially increased compared to the high concentration inflow water. These results also support the indications of (Palmer et al., 2015) that there is an increased risk of contaminant leaching after mine closure.

Khan (2020) studied the challenges in using natural peatlands for treatment of mining-influenced water and conducted research in both laboratory conditions and the natural environment. As already previously noted by other studies they also found that the changes in inflow water composition from high concentration to low concentration has an impact on the removal of contaminants from mining-influenced water towards leaching of contaminants from peat. One of the findings of the laboratory conditions part was that out of the three contaminants researched (As, Sb and Ni) antimony was more prone to leaching once the change in the inflow water composition happened. Even though nickel was not in the focus of this study, the results showed that antimony seemed to be more prone to leaching than arsenate and thus cannot be concluded that at least partially this study supports the earlier findings (Khan, 2020). These laboratory scale batch findings were also validated in later field studies as Khan concluded that the dilution of inflow water is a possible trigger for the contaminant mobilization.

Antimony is considered hazardous for human health (STM 461/2000) and arsenic in drinking water is a global problem, their health effects have been extensively studied. Arsenic is a human carcinogen (IARC, 2012). In a mining point of view all these findings in this thesis and other research from the field indicate that, if the mine's treatment peatland leaches to the nature, it may result serious danger for the nature and human health. Mining is an important industry with generally positive social impact on the local people and businesses (Kauppila et al. 2011). Because of the positive impact on local people and business it should be also very important to keep the nature safe as possible. As a recommendation, treatment peatlands can be in use for a time they do not begin to leach to nature and operate safely. However, the treatment peatlands should not operate at all after leaching begins. Leaching antimony and arsenic to nature does not benefit mine's stakeholders or the ecosystem in terms of sustainability. It is a priority and

essential to understand even more accurately the durability of treatment peatlands when using them in mining.

6 CONCLUSIONS

This study researched the remobilization of bound arsenic and antimony in peat over time as the chemical composition of the inflow water was diluted from high concentration inflow to low concentration inflow. The study was conducted in laboratory conditions by analyzing the leaching of arsenic and antimony through 8 peat columns. High concentration inflow water was first run through the peat columns and the changed to a low concentration inflow water. The leaching of antimony and arsenic was then inferred by two different methods: CP mass spectrometry (for measurement of concentrations in peat) and colorimetric determination of concentrations in water.

The results of this study supports the previous findings in this study field, that the change in the chemical composition in the inflow water from high concentration to low concentration remobilizes the contaminants (arsenic and antimony) bound in the peat and increases the leaching of these contaminants. It was found that once the inflow water was changed to low concentration water the highest concentration point in peat for both arsenic and antimony moved further away from the inflow point. For antimony this finding was confirmed by measurement of concentrations in both peat and water and for arsenic this was confirmed by the concentrations in peat and partially supported by the concentration in porewater. It was also found that the diluted inflow water did not only move the highest antimony concentration point in peat further away from the inflow point but as exposure time increased it also increased the absolute antimony concentration amounts leached to the outflow.

Findings of this study improve the understanding of contaminant leaching (antimony and arsenic) and the peat gaining a higher concentration of contaminants over time while the mine is still operational. Over time this may result in pollution in the nature, when the leaching continues from the treatment peatlands even further to soils, rivers and lakes. When the concentrations of contaminants in the aforementioned will rise to toxic levels, they will influence negatively to biodiversity in general. This is why a priority in point of sustainability should be to keep the treatment peatlands in good condition. By this, the concentrations in peat should not be allowed to increase to a point where contaminants could leach when the mine is still operational.

In the future research consideration on what might be the best ways to prevent the accumulation of contaminants in treatment peatlands should be prioritized. In addition, more ways to understanding the treatment peatlands way of working should be studied. In the eyes of mining industry, the use of treatment peatlands can't be stopped immediately, meanwhile this information about the span of time for which treatment peatland remain safe for use would be useful for the industry and safe for nature. To understand and to improve the use of peatlands for treatment of mining influenced water the knowledge of the different processes involved is required. This means, that different science field (chemistry, biology, engineering & etc.) professionals should contribute and work together for the research of a better understanding of the accumulation of contaminants in treatment peatlands. Only accurate knowledge of the accumulation of contaminants in treatment peatlands will lead to safe and optimized use of peatlands for mining influenced water.

Based on all the results analyzed can be stated that this study strongly supports the original hypothesis of this study: *Reduced arsenic/antimony level in inflow water will lead to remobilization and redistribution of the bound contaminants in the peat columns which will be observable as a flattening off and traveling of the peak concentration of bound contaminant.*

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